

Abstract

The utilization of CO as an alternate feed stock for the manufacture of specialty as well as bulk chemicals received attention due to the oil crisis in seventies. In recent years, the use of CO has gained considerable importance in the development of C1 chemistry and related carbonylation processes. The availability of CO in abundant quantities from resources such as natural gas, coal and biomass has led to this development of new routes for a wide range of chemicals. The synthesis of methanol and liquid hydrocarbons from CO and H₂, the hydroformylation of olefins, carbonylation of methanol to acetic acid and methyl acetate to acetic anhydride are some of the important processes using CO and practiced on a large scale. A vast literature on this subject dealing with new catalysts, their applications in industries and future prospects is available in several monographs and reviews [Parshall (1980), Falbe (1980), Sheldon (1983) and Keim (1988)]. While, the feasibility of a variety of carbonylation reactions has already been established, various aspects, such as the role of different types of metal complex catalysts, promoters, solvents and co-catalysts on the activity and selectivity of these reactions needs to be further investigated. Also, for many of these reactions, understanding of the reaction mechanism and kinetics is incomplete. Such studies would be extremely useful not only in developing new catalyst systems, but also in improving the selectivity and optimum operations of the existing ones. Basic research on carbonylation reactions would also be useful in further understanding of the homogeneous or heterogeneous transition metal catalysts. Therefore, the aim of this work was to investigate some fundamental aspects of carbonylation reactions by transition metal catalysis.

The following problems were investigated : ? Carbonylation of methanol to acetic acid using homogeneous nickel-isoquinoline complex catalyst : Effect of ligands, kinetic study and batch reactor model. ? Carbonylation of ethanol using homogeneous nickel complex catalysts with alkyl iodide and alkali metal iodide promoters : Activity, selectivity and kinetic study. ? Carbonylation of methyl acetate to acetic anhydride using a nickel complex catalyst: Kinetic study. ? Carbonylation of alcohols to give the corresponding carboxylic acids is an industrially important process. The carboxylic acids find widespread use in the preparation of polymers, cosmetics, poultry feed, insecticides etc. The process for the carbonylation of methanol has been commercialised using Rh catalyst. But considering the high cost of rhodium and its limited resources, there is a need for developing new processes using cheaper catalysts with high activity and selectivity. It is with this objective that the present work was undertaken on the activity and selectivity of catalysts consisting of nickel complexes. A brief summary of work done is summarised below.

Chapter 1 presents a literature survey on carbonylation of alcohols. A variety of catalysts [both homogeneous as well as heterogeneous] consisting of transition metals such as Rh, Ir, Co, Pd, Ru, Ni etc. can be used for carbonylation of alcohols. Carbonylation of alcohols using Rh and Ir catalysts has been studied in detail. Various aspects such as kinetics and mechanism, effect of various process parameters on the activity and selectivity and role of solvents and promoters have been discussed. Ni, Co and Ru are known to be poor catalysts for carbonylation of alcohols. Recently, it has been shown that Ni catalysts when modified with suitable promoters and ligands give high activity and selectivity for carbonylation of methanol [Rizkalla (1987), Kelkar (1990)]. Therefore, further work is necessary to understand the role of ligands, promoters and solvents on the activity and selectivity. Also, very little information is available on the kinetics and reaction mechanism for nickel catalysed carbonylation of alcohols. Based on the previous work, the scope

and objectives of the present work have been outlined.

Chapter 2 presents an experimental study on the carbonylation of methanol to acetic acid using a Ni complex catalyst with methyl iodide as a promoter. Various bidentate ligands containing N- or P- groups were tested for their activity and selectivity. It was observed that the activity and selectivity obtained with the bidentate ligands were comparable with isoquinoline and PPh₃. Therefore, for all further work isoquinoline was chosen as a ligand. Various transition metal catalysts such as Rh, Ir, Co, Fe and Ru were tested for their activity in the presence of isoquinoline and hydrogen (as a promoter) in order to compare their activities with Ni-isoquinoline catalyst system. Kinetic studies were done in a temperature range of 478-508 K in order to develop a rate equation. The effect of concentration of methanol, catalyst, methyl iodide, water, CO and hydrogen partial pressure on the rate of reaction was studied and a rate equation of the following form has been proposed.

$$r = k_0 A_1 C_1^{0.89} E^{0.9} (1 + 0.0014 D_1)^{0.9} (1 + K_A A_1) (1 + K_B B_1) (1 + K_P P_1)^2$$

The activation energy was calculated and found to be equal to 5.88×10^4 kJ/kmol. Based on the reaction mechanism proposed by Nelson et.al, (1986) for the carbonylation of methanol to acetic acid, a rate equation was derived which is consistent with the observed trends of variation of rate with catalyst, iodine and methyl acetate concentrations. The effect of water and hydrogen is however not explained by this model. Finally a batch reactor model has been proposed and the applicability of the rate equation to predict integral concentration-time data has been verified.

In Chapter 3, results on the carbonylation of ethanol using a nickel-isoquinoline complex catalyst are presented. Effect of catalyst precursors, ligands, iodide promoters, co-catalysts and solvents on the activity and selectivity have been studied. In all the cases the selectivity to propionic acid was found to be > 95 %. The effect of various N- and P- containing ligands on the activity and selectivity of the catalyst was studied and it was found that isoquinoline showed the best activity and selectivity. Hydrogen was found to promote the reaction without affecting the selectivity.

When SnI₂ or Lil was used as co-catalysts along with HI as a promoter, a very high activity (28×10^{-2} kmol/kg/hr) was obtained (average activity with HI : 19.73×10^{-2} kmol/kg/hr). When only Lil was used as a promoter (instead of HI), improved activity and selectivity were observed. The effect of isoquinoline concentration, HI concentration, ethanol concentration, CO partial pressure, hydrogen partial pressure, water concentration and temperature on the activity and selectivity were studied in a temperature range of 488-518 K. One of the important observations made in this work was that the formation of ethane and ethylene increases at higher HI concentrations which leads to a drop in selectivity towards propionic acid. Recycle experiments carried out showed that the catalyst activity was maintained even after four recycles. The use of Lil as a promoter is advantageous due to its non-volatile nature. Thus, a detailed study using this promoter was carried out and the results are presented in the next chapter.

Chapter 4 presents a study on the activity and selectivity of homogeneous Ni-isoquinoline complex catalyst with non-volatile alkali metal iodide (Lil) as a promoter in carbonylation of methanol, ethanol and n-propanol. The activity of Ni-isoquinoline catalyst in carbonylation of methanol was found to be marginally lower with Lil as a promoter compared to HI as a promoter while the selectivity was comparable. With ethanol and n-propanol as the substrates, the activity as well as the selectivity increases when alkyl iodide promoters were replaced by Lil as a promoter. The formation of alkane and alkene, in the case of ethanol and n-propanol were suppressed by the use of Lil as a promoter, thereby improving the selectivity towards carboxylic acids. For n-propanol, n- and iso-butyric acids were formed with 90% selectivity in the presence of Lil as a promoter. The n/iso ratio with HI as a promoter was found to be 0.67, while that with

Lil as a promoter it was 1.6. The important observations made in ethanol and n-propanol carbonylation with Lil as a promoter are :

1) Increase in the concentration of metal iodide promoter increases the activity as well as the selectivity of the catalyst. 2) The activity of the catalyst is enhanced in the presence of hydrogen. 3) The amount of alkyl iodide formation was significantly lower in presence of metal iodide compared to HI as a promoter. The activity and selectivity studies for ethanol carbonylation were carried out using Lil as the promoter in a temperature range of 498-518 K. The effect of catalyst concentration, Lil concentration, ethanol concentration, CO partial pressure, hydrogen partial pressure, water concentration and temperature on the activity and selectivity of the reaction was also studied. The important observation made for ethanol carbonylation with Lil as a promoter are:

1) The rate of reaction increases linearly with increase in catalyst and Lil concentrations. 2) The rate of reaction increases first and then remains constant with increase in ethanol concentration and CO partial pressure. 3) The rate of reaction decreases with increase in water concentration. 4) The rate of reaction increases with increase in hydrogen partial pressure. Catalyst recycle studies were carried out for carbonylation of ethanol using Niisoquinoline catalyst with Lil as a promoter. It was observed that the activity of the catalyst is retained upto two recycles after which it decreases with each recycle. The loss in activity was mainly due to the loss of Ni as Ni(CO)₄. Based on the observed results, mechanistic feature of the reaction are discussed.

Chapter 5 presents a kinetic study of carbonylation of ethanol using Niisoquinoline catalyst system. The aim of this work was to compare the kinetics of this reaction with HI and Lil as promoters. Kinetic study of carbonylation of ethanol using Ni-isoquinoline-HI catalyst system has been discussed. For this purpose the experiments were carried out to observe the initial rate of reaction as a function of catalyst concentration, agitation speed, ethanol concentration, HI concentration, hydrogen partial pressure and CO partial pressure. The important observations made in this work were: 1) Agitation speed has no influence on the rate of reaction, indicating that the reaction was kinetically controlled in the range of conditions studied. 2) The rate of reaction increases linearly with increase in catalyst concentration. 3) The rate of reaction increases with increase in HI concentration, but with further increase, the rate drops sharply. 4) The rate of reaction increases with increase in ethanol concentration and remains constant at higher concentrations. 5) The rate of reaction decreases with increase in water concentration. 6) The rate of reaction increases with increase in CO partial pressure and remains constant at higher values. 7) The rate of reaction increases with increase in hydrogen partial pressure and remains constant at higher pressure. Based on these observations a rate equation was proposed and kinetic parameters were evaluated. The following form of rate equation was found to represent the data satisfactorily.

$$R = \frac{k_0 A \cdot B^{1-\alpha} C^{1-\beta} D^{\gamma}}{(1 + K_A A)(1 + K_B B)(1 + K_E E)^3 (1 + K_P P)^2}$$

The energy of activation was found to be 5.28 x 10⁴, kJ/kmol. Kinetic study on carbonylation of ethanol using Ni-isoquinoline-Lil catalyst system was studied. The observations made in this study were similar to that observed in the case of HI promoter. The main difference observed was with respect to Lil as a promoter. It was observed that the rate of reaction increases linearly with increase in Lil concentration. In contrast, with HI as a promoter, the rate of reaction increases initially and at higher concentrations, the rate drops sharply. A rate equation of the following form was found to represent the data satisfactorily

$$R = \frac{k_0 A \cdot B^{1-\alpha} C^{1-\beta} D^{\gamma}}{(1 + K_A A)(1 + K_B B)(1 + K_P P)^2}$$

The energy of activation was found to be 5.00×10^4 , kJ/kmol

In Chapter 6, results on carbonylation of methyl acetate to acetic anhydride are presented using a homogeneous Ni-isoquinoline complex catalyst. The first part of this work deals with the literature survey on carbonylation of methyl acetate. Various transition metals such as Rh, Ir, Ru and Ni have been reported as catalysts for carbonylation of methyl acetate. The literature shows that the previous work on the kinetics and mechanism of carbonylation of methyl acetate is limited to rhodium and iridium catalyst systems. Ni complex catalyst were also found to be active for this reaction at higher temperatures and pressures (453-463 K and $6.5 \times 10^4 - 7 \times 10^4$ kPa). Recently it has been shown that when Ni salts with N- or P- containing ligands are used as catalysts, the reaction was feasible at milder conditions. This catalyst has potential importance in acetic anhydride manufacture as it is based on a cheaper Ni complex catalyst unlike the expensive Rh catalyst in the Tennessee Eastman process. Therefore, it was thought important to investigate Ni catalysed carbonylation of methyl acetate. The scope and objectives of this work are outlined in the first part.

In the second part of this chapter, results on the effect of ligands, solvents, cocatalysts and promoters on the average activity and selectivity of the Niisoquinoline catalyst are discussed. The rate data at different conditions have also been presented. The following rate equation has been proposed:

$$R_A = \frac{0.07 E_0.61 (1 + 0.0597 D_0.7931) R_A}{(4) (1 + K_B B_1) (1 + K_F F_1)^2}$$